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Some Equilibria Aspects of KDP Growth Solutions

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September 30, 2014

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This work performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract DE-AC52-07NA27344.

Interdepartmental letterhead
Mail Station L-491
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MEMORANDUM – May 20, 2003

NIF0101124/adf

TO: File

FROM: P.E. Miller

SUBJECT: Some Equilibria Aspects of KDP Growth Solutions

Introduction

Single crystal potassium dihydrogen phosphate (KDP), such as that used for optical harmonic generation is typically grown from aqueous solutions. In addition to water and KDP, a variety of trace level materials are typically present in KDP growth solutions. For example metallic species, such as aluminum, are sometimes intentionally added in an attempt to control the aspect ratio of the crystal. Other metallic cations may be present as the result of leaching from materials that are used in the construction of the crystallizer, or because of impurities present in the KDP or aqueous growth media.

The raw material typically used for the growth of single crystal KDP is generally prepared¹ by precipitating KDP from an aqueous solution containing H₃PO₄, KOH and about 1 mole% of the dipotassium salt of ethylenediaminetetraacetic acid. The EDTA is used during the preparation of the KDP feedstock as a means of sequestering trace quantities of metallic species, such as iron, which are invariably present in the raw materials. During the precipitation of the KDP feedstock, a small fraction of the EDTA either co-precipitates or adsorbs to the surface of the KDP crystals. Thus growth solutions using “low impurity” KDP prepared by this method generally contain a small fraction of EDTA.

The presence of adsorbed materials, originating from the preparation of the KDP feedstock, can potentially affect the KDP crystallization process. For example, if sufficient EDTA were present it could potentially complex with metallic cations, such as Al³⁺, that are sometimes used to control the aspect ratio of KDP crystallization. It is reasonable to expect that, if this were the case, then not all aluminum species would be expected to be incorporated into the crystal lattice. Altering the speciation of metallic complexes by the introduction of EDTA could perturb the relative growth rates of the various crystal faces. Alternatively, it is possible that the presence of adsorbed species could also alter the equilibrium pH (hydrogen ion concentration) of KDP solutions. Such a change in hydrogen ion concentration would result in a change in the equilibrium solubility, and thus the supersaturation of solutions used for KDP growth.

It is not immediately obvious what the magnitude of such effects might be. Therefore, in the present document we will develop a number of expressions that can be used to estimate the size of

¹ R. Roza and R. Torres EDTA Method for Synthesis of Low Impurity KDP. Internal Memo Dated August 10, 1998.

these effects. For convenience, in the present document, we have made a number of simplifications. For example, thermodynamic constants are typically reported in the literature at a variety of different ionic strengths. For the present we have not been rigorous in adjusting these values to a consistent ionic strength characteristic of the solution of interest. A more detailed treatment incorporating activity coefficients can be performed in the future should the present results suggest that such a refinement would be of value. Further it should be emphasized that the present approach considers only thermodynamics; kinetics are not considered. For many reactions, such as those involving proton transfer, it is probably reasonable to assume that kinetic inhibitions are unlikely. In some cases, such as the formation of some metallic EDTA complexes, kinetic considerations may be of importance at low temperatures. However, the formation of metallic EDTA complexes of most interest, in the present work, appear to be thermodynamically favored at high rather than low temperatures.

We will begin by considering the acid-base behavior of pure KDP solutions and the effect that changes in the hydrogen ion concentration would be expected to have on the equilibrium solubility of KDP. This will be followed by an examination of the speciation of aluminum in KDP solutions both in the absence and the presence of EDTA. Finally we will briefly examine the solubility limit of Al in a saturated solution of KDP.

Equilibrium Concentration of $[H^+]$ in Aqueous KDP Solutions

When potassium dihydrogen phosphate (KDP) dissolves in aqueous solution the dihydrogen phosphate $H_2PO_4^-$ anion is immediately formed. This anion is amphoteric; capable of acting both as a Lowry-Bronsted acid (i.e. a proton donor) or as a Lowry-Bronsted base (i.e. as a proton acceptor). In aqueous solution, the $H_2PO_4^{2-}$ anion has the potential to undergo the following acid/base reactions:

Acidic Reactions:



Basic Reactions:



Similarly, water also acts as a source of both hydroxide ions and protons owing to its self-dissociation:



With respect to the $H_2PO_4^-$ anion, any time a protonated species, such as H^+ or H_3PO_4 , is formed in solution; one of the conjugate bases (i.e. HPO_4^{2-} , PO_4^{3-} , OH^-) must also be formed. By balancing the *protons* in Equations 1-4 one finds:

$$[H^+] + [H_3PO_4] = [OH^-] + [HPO_4^{2-}] + 2[PO_4^{3-}] \quad 5)$$

Note that for each mole of PO_4^{3-} that is formed, two moles of protons are released by Equation 2.

In the absence of species other than KDP and water, it is clear that any phosphate species in solution is the result of the initial formation of the $\text{H}_2\text{PO}_4^{2-}$ anion or its subsequent reaction via Equations 1-3. That is, one can define the total or analytical concentration $^P C_T$, of all phosphate species as:

$$^P C_T = [\text{H}_3\text{PO}_4] + [\text{H}_2\text{PO}_4^-] + [\text{HPO}_4^{2-}] + [\text{PO}_4^{3-}] \quad (6)$$

Having defined the total phosphate concentration $^P C_T$ one may define the fractional abundance of each of the individual phosphate species with respect to the total concentration $^P C_T$:

$$\alpha_0 = \frac{[\text{H}_3\text{PO}_4]}{[\text{H}_3\text{PO}_4] + [\text{H}_2\text{PO}_4^-] + [\text{HPO}_4^{2-}] + [\text{PO}_4^{3-}]} = \frac{[\text{H}_3\text{PO}_4]}{^P C_T} \quad (7)$$

$$\alpha_1 = \frac{[\text{H}_2\text{PO}_4^-]}{[\text{H}_3\text{PO}_4] + [\text{H}_2\text{PO}_4^-] + [\text{HPO}_4^{2-}] + [\text{PO}_4^{3-}]} = \frac{[\text{H}_2\text{PO}_4^-]}{^P C_T} \quad (8)$$

$$\alpha_2 = \frac{[\text{HPO}_4^{2-}]}{[\text{H}_3\text{PO}_4] + [\text{H}_2\text{PO}_4^-] + [\text{HPO}_4^{2-}] + [\text{PO}_4^{3-}]} = \frac{[\text{HPO}_4^{2-}]}{^P C_T} \quad (9)$$

$$\alpha_3 = \frac{[\text{PO}_4^{3-}]}{[\text{H}_3\text{PO}_4] + [\text{H}_2\text{PO}_4^-] + [\text{HPO}_4^{2-}] + [\text{PO}_4^{3-}]} = \frac{[\text{PO}_4^{3-}]}{^P C_T} \quad (10)$$

Using this notation and expressing the hydroxide concentration in terms of the hydrogen ion concentration and the equilibrium constant associated with the self dissociation of water (K_w), allows one to recast the proton balance (Equation 5) as:

$$[\text{H}^+] + \alpha_0 ^P C_T = \frac{K_w}{[\text{H}^+]} + \alpha_2 ^P C_T + 2\alpha_3 ^P C_T \quad (11)$$

By examining the series of simultaneous equilibria from Equations 1-4, it is easy to see that the fractional abundance of any one of the phosphate species will depend on two factors. The first factor of importance is the extent to which each of the reactions takes place. This factor is summarized by the equilibrium constant associated with each of the reactions. The second factor, of importance, is the equilibrium hydrogen ion concentration of the solution in which the reactions take place. In general, the fractional abundances defined in Equations 7-10 are easily shown² to depend on the successive acid dissociation constants (K_1 , K_2 , and K_3) and the hydrogen ion concentration in the following way:

$$\alpha_0 = \frac{[\text{H}^+]^3}{[\text{H}^+]^3 + K_1[\text{H}^+]^2 + K_1K_2[\text{H}^+] + K_1K_2K_3} \quad (12)$$

² H. Frieser and Q. Fernando *Ionic Equilibria in Analytical Chemistry*, John Wiley and Sons New York 1963

$$\alpha_1 = \frac{K_1[H^+]^2}{[H^+]^3 + K_1[H^+]^2 + K_1K_2[H^+] + K_1K_2K_3} \quad (13)$$

$$\alpha_2 = \frac{K_1K_2[H^+]}{[H^+]^3 + K_1[H^+]^2 + K_1K_2[H^+] + K_1K_2K_3} \quad (14)$$

$$\alpha_3 = \frac{K_1K_2K_3}{[H^+]^3 + K_1[H^+]^2 + K_1K_2[H^+] + K_1K_2K_3} \quad (15)$$

Substituting Equations 12, 14 and 15 into Equation 11 allows the proton balance to be written as:

$$\begin{aligned} [H^+] + \left\{ \frac{[H^+]^3}{[H^+]^3 + K_1[H^+]^2 + K_1K_2[H^+] + K_1K_2K_3} \right\} {}^pC_T = \\ \frac{K_w}{[H^+]} + \left\{ \frac{K_1K_2[H^+]}{[H^+]^3 + K_1[H^+]^2 + K_1K_2[H^+] + K_1K_2K_3} \right\} + \\ 2 \left\{ \frac{K_1K_2K_3}{[H^+]^3 + K_1[H^+]^2 + K_1K_2[H^+] + K_1K_2K_3} \right\} {}^pC_T \end{aligned} \quad (16)$$

Equation 16 is a general expression that relates the hydrogen ion concentration, the analytical concentration of dihydrogen phosphate and a series of thermodynamic equilibrium constants. Given the appropriate, temperature dependent equilibrium constants one can solve Equation 16 and thus obtain the equilibrium concentration of H^+ at arbitrary values of pC_T and temperature.

In the special case of a saturated solution, the phosphate concentration is given by the solubility of KDP. Combining empirical expressions for the solubility³, given in units of grams KDP/ 100 grams of solution, and the density⁴ of saturated solutions of KDP, and recognizing that the molecular weight of KDP is 136 grams/mole it is easy to show that the molarity of a saturated aqueous solution of KDP (${}^{KDP}S$) is given as a function of temperature, T (in °C) by:

$${}^{KDP}S = (10/136)[12.79 + .250T + 8.2 \times 10^{-3}T^2 + 6.16 \times 10^{-6}T^3] \times [1.08 + 2.63 \times 10^{-3}T] \quad (17)$$

The equilibrium constants for the stepwise dissociation of phosphoric acid, together with the associated heats of reaction (ΔH) are given in Table 1. Use of the heat of reaction allows one to calculate change in the equilibrium constant as a function of temperature⁵ (T). In the general case this dependence can be summarized as:

$$\frac{d \ln(K)}{dT} = \frac{\Delta H(T)}{RT^2} \quad (18)$$

³ L.N. Rashkovich *KDP-Family Single Crystals* Adam Hilger Press 1991, page 19

⁴ L.N. Rashkovich *KDP-Family Single Crystals* Adam Hilger Press 1991, page 25

⁵ P.W. Atkins *Physical Chemistry 2nd Edition* WH Freeman and Co. 1978, page 268

For moderate changes in temperature one can treat $\Delta H(T)$ as a constant. Using this approximation, when ΔH is expressed in kcal/mole, and base 10 logarithms are used, then the near 25 °C (298 K) the equilibrium constant (K_2) at temperature T_2 is related to the equilibrium constant K_1 at temperature T_1 by:

$$\log(K_2) \approx \log(K_1) + .00246 \Delta H (T_2 - T_1) \quad 19)$$

Table 1: Equilibrium Constants⁶ for Stepwise Dissociation of Phosphoric Acid. All data are given at 25 °C.

Reaction	pK	ΔH (kcal/mole)	$\Delta \log(K)/^\circ C$
$H_3PO_4 = H^+ + H_2PO_4^-$	1.74	-2.10	-0.0052
$H_2PO_4^- = H^+ + HPO_4^{2-}$	6.44	1.00	+0.0025
$HPO_4^{2-} = H^+ + PO_4^{3-}$	11.25	4.70	+0.0116
$H_2O = H^+ + OH^-$	14.0	13.41	+0.0330

Using the constants shown in Table 1, and Equations 17, and 19 one can estimate the acid dissociation constants and the phosphate concentration as a function of temperature. One can then determine the hydrogen ion concentration as a function of temperature by iteratively solving Equation 16. As shown in Figure 1, the hydrogen ion concentration of a pure saturated solution of KDP is nearly constant over the temperature ranges of interest, becoming very slightly more basic as the temperature of the solution is raised.

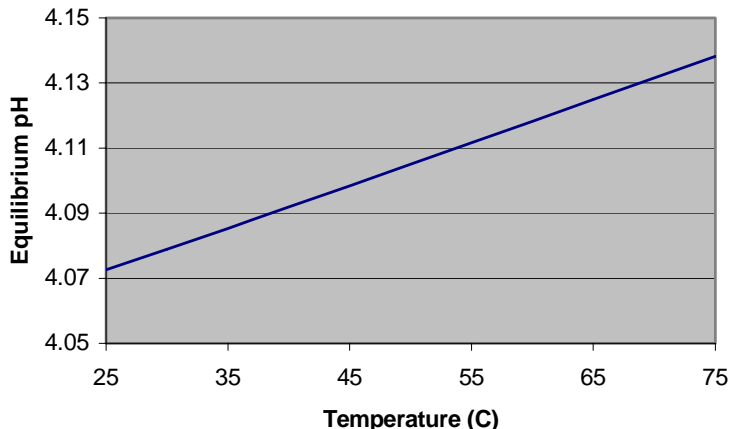


Figure 1: Equilibrium pH of a saturated solution of KDP as a function of temperature.

Again referring to Figure 1, at 25 °C a saturated solution of KDP has a pH of ≈ 4.07 . In Figure 2 the relative distribution of each of the phosphate species (H_3PO_4 , $H_2PO_4^-$, HPO_4^{2-} , and PO_4^{3-}) have been plotted as a function of the pH of the solution. As one might expect, at the equilibrium pH of dissolved KDP, the dominant phosphate species is the dihydrogen phosphate anion. Because the equilibrium concentration of both phosphoric acid (H_3PO_4) and the hydrogen phosphate HPO_4^{2-} anion (e.g. the corresponding weak acid or conjugate base of the amphoteric dihydrogen

⁶ R.M Smith and A.E. Martell, *NIST Critically Selected Stability Constants of Metal Complexes Database Version 1* U.S. Department of Commerce, Technology Administration, National Institutes of Standards and Technology Gaithersburg, MD 20899, 1993

phosphate) are roughly 230 times lower than the dihydrogen phosphate anion, the buffer capacity of such a solution would be expected to be modest.

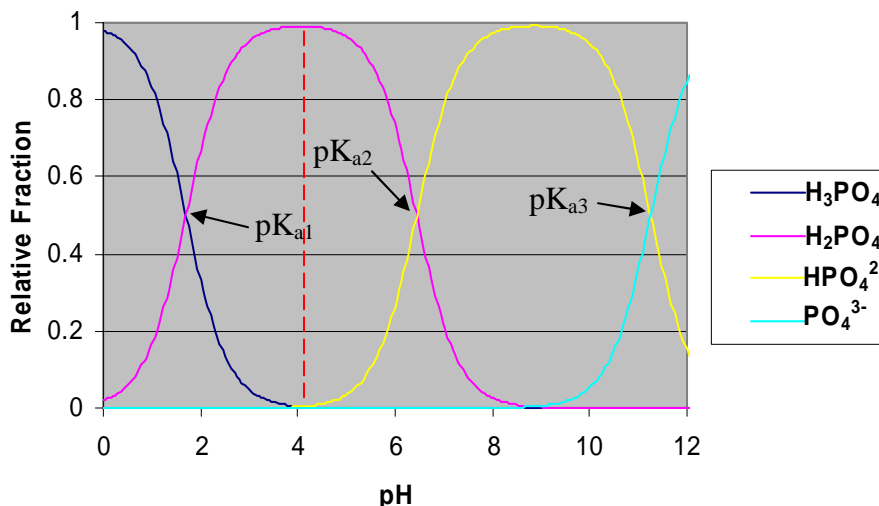
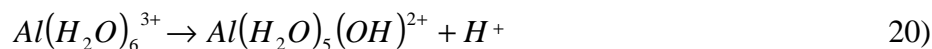


Figure 2: Relative abundance of phosphate species as a function of pH at 25 °C. The equilibrium pH of saturated KDP is shown as the vertical red dashed line. Note the ordinate is given as a linear scale.

Dependence of KDP Solubility on Hydrogen Ion Concentration

Given both the method by which high purity KDP is made and the modest buffer capacity of the growth solutions, it is of interest to examine the effect that small changes in pH might be expected to have on the equilibrium solubility, and thus the super-saturation of KDP growth solutions. There are several physical reasons that could potentially lead to small changes in the pH of KDP growth solutions. These include adsorption of gases such as CO_2 , adsorption of small quantities of excess reagents (such as H_3PO_4 or KOH) used during the preparation of the high purity KDP or even the presence of some hydrated cations which can act as a Lowry-Bronsted acids. The classic example⁷ of such phenomenon is that of the hydrated Al^{3+} cation.



The magnitude of potential changes in pH owing to any one of these effects is difficult to predict. For this reason we will simply estimate the magnitude of changes in pH that would be required to result in a change the equilibrium solubility of KDP by an amount which is significant (say 0.1% super-saturation) in comparison to that of interest during the growth of KDP.

At a given temperature, the equilibrium solubility of pure aqueous solutions of KDP can be represented by:



⁷ G.H. Farrah and M.L. Moss in *Treatise on Analytical Chemistry Part II, Volume 4*, Page 378 I.M. Koltoff and P. J. Elving (editors) Wiley Interscience 1963

Because the $\text{H}_2\text{PO}_4^{2-}$ anion is amphoteric (Equations 1-3), and given the stoichiometry of Equation 21 it is easy to see that the equilibrium solubility (^{KDP}S) of KDP can be written as:

$$^{KDP}S = [\text{H}_3\text{PO}_4] + [\text{H}_2\text{PO}_4^{2-}] + [\text{HPO}_4^{2-}] + [\text{PO}_4^{3-}] \quad (22)$$

With respect to the thermodynamic driving force associated with Equation 21, only that fraction of the total phosphate species that is in the form of the $\text{H}_2\text{PO}_4^{2-}$ anion (see Equation 8) is relevant. Thus the equilibrium solubility of KDP would be expected to increase as more of the $\text{H}_2\text{PO}_4^{2-}$ anion was converted to either H_3PO_4 (more acidic conditions) or HPO_4^{2-} (more basic conditions). Specifically, the equilibrium solubility is found to vary in proportion to the inverse square root of the fractional abundance of the $\text{H}_2\text{PO}_4^{2-}$ anion:

$$^{KDP}S = \left[\frac{^{KDP}K_{sp}}{\alpha_1} \right]^{1/2} = \left[\left(\frac{^{KDP}K_{sp}}{K_1[\text{H}^+]^2} \right) \left([\text{H}^+]^3 + K_1[\text{H}^+]^2 + K_1K_2[\text{H}^+] + K_1K_2K_3 \right) \right]^{1/2} \quad (23)$$

Where $^{KDP}K_{sp}$ is the equilibrium constant (solubility product) associated with Equation 21.

Given this, it is easy to see that the equilibrium solubility of KDP would be expected to increase as one deviates from the equilibrium pH. Such a change in equilibrium solubility translates directly into a change in super-saturation. From Figure 3, it is easy to see that a change in pH of about 0.3 units (e.g. a change in H^+ concentration by a factor of 2) would decrease the super-saturation by about 0.1%, while a shift in pH of 0.6 units would lower the super-saturation by about 0.5%. Changes in pH of this magnitude are plausible, but have not been observed in LLNL growth solutions to date.

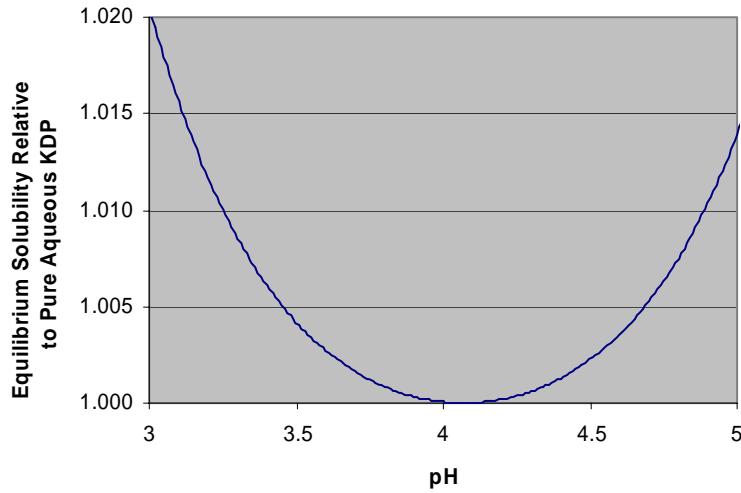
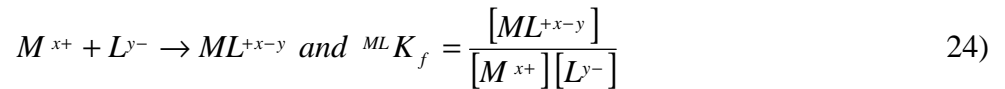


Figure 3: The effect of changes in solution pH on the equilibrium solubility of KDP at 25 °C. Note that the equilibrium solubility of KDP increases by about 0.1% for a change in pH of approximately 0.3 pH units. Similarly a change of 0.6 pH units results in a change in the equilibrium solubility of approximately 0.5%.

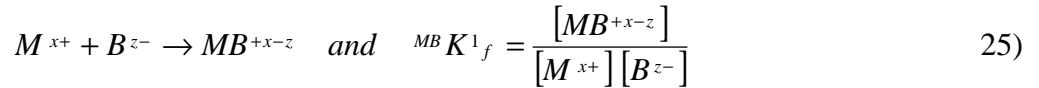
Trivalent cations such as Fe^{3+} , Cr^{3+} and Al^{3+} have been shown to preferentially retard or pin the growth of the prismatic face of KDP crystals. For this reason such cations have been used as one means of controlling the aspect ratio of single crystal KDP during their growth⁸. Different species of the same metallic element would be expected exhibit profound differences with respect to their ability to be incorporated into or influence the aspect ratio of a crystal. Given this, the particular chemical form of metal cations, such as aluminum, in solution is of interest. This is particularly true in those growth solutions which are prepared using “low impurity” KDP and thus have the potential to contain residual EDTA.

With respect to metal speciation, it is useful to consider any hydrated metallic species as a Lewis acid. That is, the electron deficient cation functions as a polybasic species that is capable of coordinating with as many (Lewis) bases (i.e. electron donors) as can be accommodated in the coordination sphere of the cation. Thus the question of metallic speciation can be viewed as an issue of the relative stability of the various complexes that can be formed between a metal cation and whatever Lewis bases might be available in the growth solution.

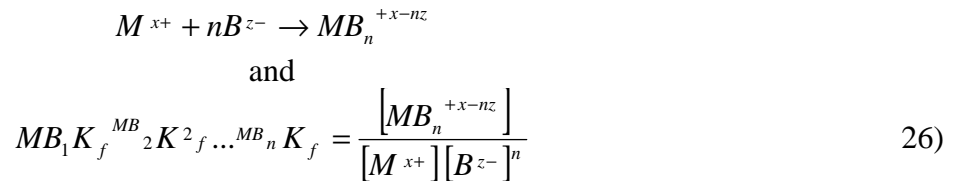
Let us begin a quantitative examination of such a competition by considering the general case of two competing Lewis bases, L^{y-} , and B^{z-} that form complexes with the Lewis acid M^{x+} . The chemical reaction and the associated equilibrium expression for the complexation with L^{y-} can be written as:



Let us further assume that M^{x+} will coordinate with multiple ligands (B^{z-}). For the first coordination reaction involving B^{z-} one can write:



While in general, for subsequent coordination reactions one can write:



Where ${}^{\text{MB}}K_{1f}$, ${}^{\text{MB}}K_{2f}$, and ${}^{\text{MB}}K_{nf}$ are the *stepwise* formation constants associated with the complexation one, two and n units of the Lewis base (B^{z-}) with the metal cation M^{x+} . Alternately, one can express Equation 26 in terms of the overall formation constant, which is the product of each of the stepwise formation constants.

The total concentration ${}^{\text{M}}\text{C}_T$ of all species of the metallic cation M, such as one might measure experimentally by plasma spectrometry, can be written as:

⁸ L.N. Rashkovich *KDP Family of Crystals* Adam-Hilger Press, 1991 page 143

$${}^M C_T = [M^{n+}] + [ML^{+x-y}] + [MB^{+x-z}] + \dots + [MB_n^{+x-nz}] + \dots \quad (27)$$

The concentration of each of the metallic species of shown in Equation 27 can be expressed as a function of the concentration of the hydrated metallic ion by rearranging the equilibrium expressions associated with Equations 24, 25 and 26. By substitution into Equation 27 it is easy to show:

$${}^M C_T = [M^{n+}] \left\{ 1 + {}^{ML} K_f [L^{y-}] + {}^{MB} K_f [Bz] + \dots + {}^{MB_1} K_f {}^{MB_2} K_f \dots {}^{MB_n} K_f [B^{z-}]^n + \dots + \dots \right\} \quad (28)$$

Many Lewis bases are also Lowry-Bronsted bases. In such cases one must also consider the speciation of the ligand, in that only that fraction (α) of the total concentration (${}^L C_T$) of a ligand that is in the chemical form that participates in the chemical reaction is of thermodynamic significance. Thus one can write:

$${}^M C_T = [M^{n+}] \left\{ 1 + {}^{ML} K_f {}^L \alpha {}^L C_T + {}^{MB} K_f {}^B \alpha {}^B C_T + \dots + {}^{MB_1} K_f {}^{MB_2} K_f \dots {}^{MB_n} K_f ({}^B \alpha {}^B C_T)^n + \dots + \dots \right\} \quad (29)$$

In a manner analogous to the series of fractional abundances (α values) defined for species derived from Lowry-Bronsted acids (see Equations 7-10), a series of β values, corresponding to the fractional abundance of each of the metallic species in solution, can be defined. For example, the fraction of the total concentration of the metal M, (${}^M C_T$) that exists as the hydrated cation (β_o) is easily seen from Equation 29 to be:

$$\beta_o = \frac{1}{\left\{ 1 + {}^{ML} K_f {}^L \alpha {}^L C_T + {}^{MB} K_f {}^B \alpha {}^B C_T + \dots + {}^{MB_1} K_f {}^{MB_2} K_f \dots {}^{MB_n} K_f ({}^B \alpha {}^B C_T)^n + \dots + \dots \right\}} \quad (30)$$

Similarly the fraction of the species MB_n^{+x-nz} , is given by:

$$\beta_n = \frac{{}^{MB_1} K_f {}^{MB_2} K_f \dots {}^{MB_n} K_f ({}^B \alpha {}^B C_T)^n}{\left\{ 1 + {}^{ML} K_f {}^L \alpha {}^L C_T + {}^{MB} K_f {}^B \alpha {}^B C_T + \dots + {}^{MB_1} K_f {}^{MB_2} K_f \dots {}^{MB_n} K_f ({}^B \alpha {}^B C_T)^n + \dots + \dots \right\}} \quad (31)$$

As shown in Equations 30, and 31, the relative fraction of each species in solution is a function of three variable types. These include the formation constants of each of the species, the equilibrium concentration of each of the unbound ligands involved, and the fraction of each ligand that is in the chemical form that can thermodynamically drives each of the complexation reactions.

In pure KDP growth solutions there are several classes of Lewis bases that can potentially coordinate with metallic cations. The first are those ligands derived from the solvent, specifically water and the hydroxide ion. The second class of Lewis bases that must be considered are the family of phosphate anions ($H_2PO_4^-$, HPO_4^{2-} , and PO_4^{3-}) that are present due to the dissolution of KDP. In solutions prepared from "low impurity" KDP, a third Lewis base, EDTA must also be considered. The formation constants of both the hydroxides and the phosphate species are shown in Table 2.

Table 2: Formation Constants⁶ at 25 °C for Reactions of Al with Lewis Bases in KDP Solutions

Reaction	log(K _f)	Temp. °C
$\text{Al}^{3+} + \text{H}_2\text{PO}_4^- = \text{Al}(\text{H}_2\text{PO}_4)^{2+}$	4.25	37
$\text{Al}^{3+} + \text{HPO}_4^{2-} = \text{Al}(\text{HPO}_4)^+$	7.7	37
$\text{Al}^{3+} + \text{PO}_4^{3-} = \text{AlPO}_4$	15.9	37
$\text{Al}^{3+} + \text{OH}^- = \text{AlOH}^{2+}$	8.21	25
$\text{AlOH}^{2+} + \text{OH}^- = \text{Al}(\text{OH})_2^+$	8.59	25
$\text{Al}(\text{OH})_2^+ + \text{OH}^- = \text{Al}(\text{OH})_3$	7.9	25
$\text{Al}(\text{OH})_3 + \text{OH}^- = \text{Al}(\text{OH})_4^-$	6.8	25

The total concentration of Al is always much, much smaller than the concentration of water, and thus hydroxide. Therefore, the equilibrium concentrations of the hydroxide ion will be invariant with respect to the extent to which hydroxide complexation might or might not occur. Further, hydroxide ion is always in equilibrium with water and the H^+ ion (see Equation 4). Therefore, one can express the hydroxide concentration as a function of the H^+ concentration, specifically as $K_w/[\text{H}^+]$.

Similarly, the total concentration of phosphate species ($^{\text{P}}\text{C}_\text{T}$) is always much greater than the aluminum concentration. Therefore the equilibrium concentration each of the phosphate species, H_2PO_4^- , HPO_4^{2-} , and PO_4^{3-} , will depend only on the pH of the solution, rather than the extent of reaction with Al. For solutions that are near the solubility of limit of KDP, one can express the concentration of each of the species as $\alpha_1^{\text{KDP}}\text{S}$, $\alpha_2^{\text{KDP}}\text{S}$ and $\alpha_3^{\text{KDP}}\text{S}$. Where α_1 , α_2 and α_3 (see Equations 13, 14, and 15) represent the fraction of the total phosphate inventory that exists as the H_2PO_4^- , HPO_4^{2-} , and PO_4^{3-} anions (see Figure 4) as a function of pH. Again $^{\text{KDP}}\text{S}$ represents the molar solubility of KDP.

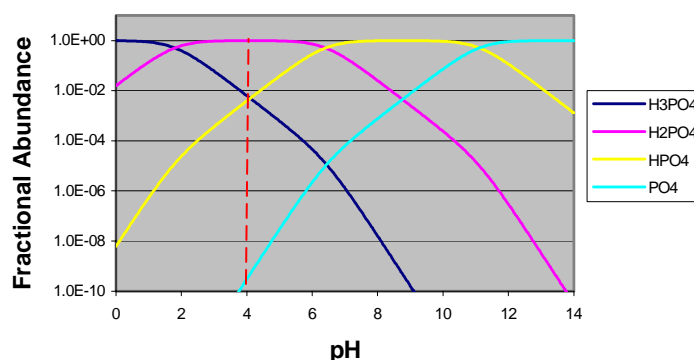


Figure 4: Relative distribution of phosphate species as a function of pH at 37 °C. The equilibrium pH of a saturated KDP solution, at this temperature (4.09) is shown as the vertical red dashed line. Note the ordinate is given as a logarithmic scale.

By substituting the formation constants found in Table 2 together with the appropriate ligand concentrations and fractional abundances into Equation 31, one can estimate the relative abundances of each of the aluminum species in the absence of EDTA (see Figure 5).

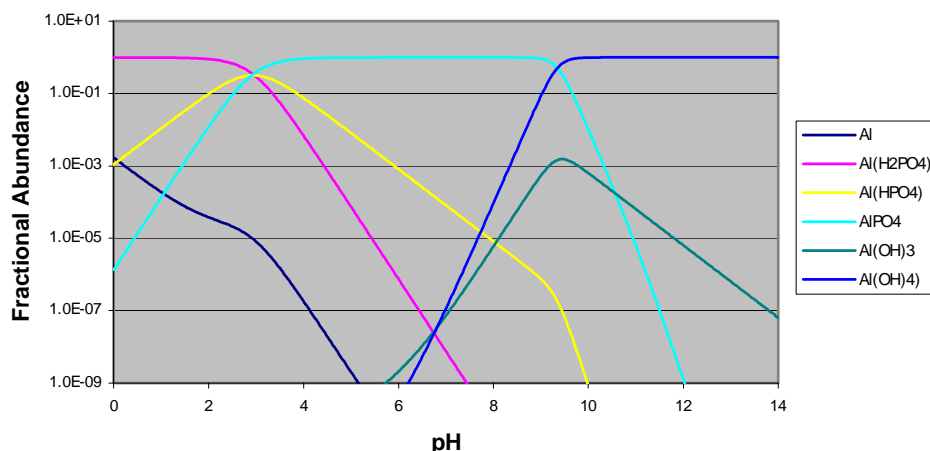


Figure 5: Schematic representation of the relative abundance of aluminum species in saturated solution of KDP. Note that at the pH of interest the dominant species are AlPO_4 , AlHPO_4^+ and $\text{AlH}_2\text{PO}_4^{2+}$.

As is shown in Figure 5, the dominant Al species in the pH ranges of interest (4.1-4.3) are AlPO_4 , AlHPO_4^+ and $\text{AlH}_2\text{PO}_4^{2+}$. Moreover the hydroxides are not present at a significant abundance until the pH exceeds about 8. This, of course, is the result of the low equilibrium abundance of the hydroxide ion at lower pHs. Thus while the formation constants used to calculate the abundance of the hydroxide species were at 25 °C and the formation constants used for the phosphates were at 37 °C it is abundantly clear that the hydroxides are of little significance at the pHs of interest.

It is interesting to note that, at a pH of 4, the abundances of the aluminum species go as $\text{AlPO}_4 > \text{AlHPO}_4^+ > \text{AlH}_2\text{PO}_4^{2+}$, which is opposite of the relative abundance of the phosphate ligands which go as $\text{H}_2\text{PO}_4^- > \text{HPO}_4^{2-} \gg \text{PO}_4^{3-}$ (see Figure 4). Such behavior is not, however, unexpected. The relative abundance of the aluminum species is dominated by the relative strength of each of the ligands as a Lewis base. Comparing Tables 1 and 2, one finds that the relative strength of the phosphates both as Lewis *and* as Lowry-Bronsted bases is $\text{PO}_4^{3-} \gg \text{HPO}_4^{2-} > \text{H}_2\text{PO}_4^-$.

Aqueous Phase Aluminum Speciation in the Presence of EDTA

As mentioned above the multidentate ligand EDTA (see Figure 6) is often used during the initial preparation of KDP feedstock. By forming a highly stable (and charged) iron EDTA complex, the solubility of iron in phosphate solutions can be increased dramatically, and thus its presence in the precipitated feedstock can be minimized. In the present section we will consider the effect that the presence of residual EDTA might be expected to have on the equilibrium distribution of soluble aluminum species.

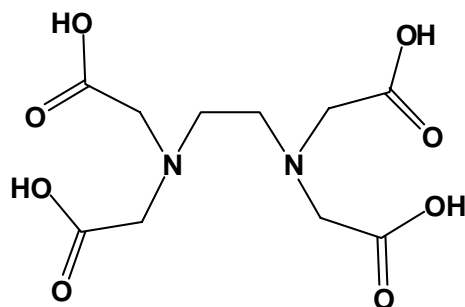


Figure 6: Structure of the protonated EDTA molecule. Note that the fully deprotonated anion can coordinate with a metallic cation at each of the four carboxylic acid sites and both of the amine functional groups.

As is evident from Figure 6, EDTA is basic both in the Lewis sense and the Lowry-Bronsted sense. The stepwise acid dissociation constants and the formation constant of the Al-EDTA complex are summarized in Table 3.

Table 3: Acid Dissociation and Formation constants⁶ for EDTA at 25 °C

Reaction	pK	log(K _f)	ΔH (kcal/mole)	Δlog(K)/ °C
$\text{H}_4\text{EDTA} = \text{H}^+ + \text{H}_3\text{EDTA}^-$	2.03		-0.30	-0.0007
$\text{H}_3\text{EDTA}^- = \text{H}^+ + \text{H}_2\text{EDTA}^{2-}$	2.61		-1.45	-0.0036
$\text{H}_2\text{EDTA}^{2-} = \text{H}^+ + \text{HEDTA}^{3-}$	6.10		5.60	0.0138
$\text{HEDTA}^{3-} = \text{H}^+ + \text{EDTA}^{4-}$	9.86		6.30	0.0155
$\text{Al}^{3+} + \text{EDTA}^{4-} = \text{Al-EDTA}^-$		16.6 ⁹	12.6	0.0310

Using the acid dissociation constants from Table 3 it is straightforward to calculate the abundance of the various EDTA species as a function of pH, using expressions that are analogous to Equations 12-15. Similarly, by using the heats of reaction and Equation 19 it is a simple matter to extend these results to any arbitrary temperature. The speciation of the proton complexes of EDTA, at 37 °C, is shown in Figure 7.

⁹ Aluminum also forms complexes with species such as the HEDTA^{3-} anion. However because EDTA^{4-} is a much, much stronger (Lewis) base than is HEDTA^{3-} it is sufficient to consider only the Al-EDTA⁻ complex for the purposes of the present work.

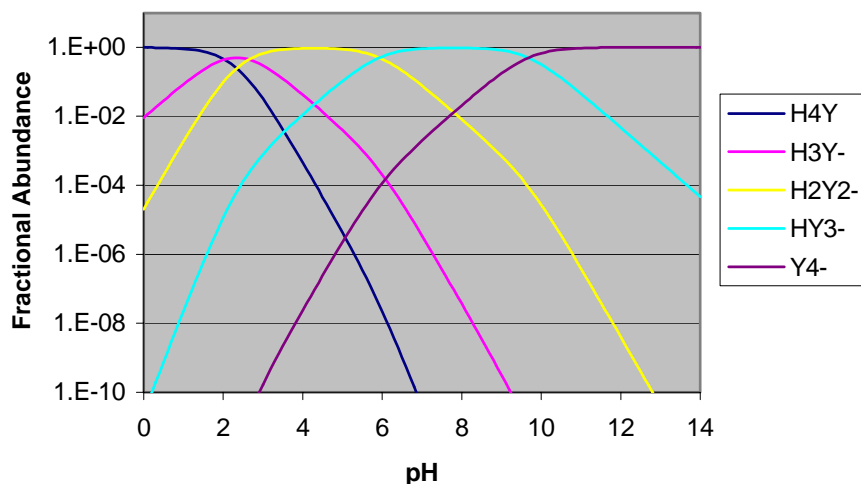


Figure 7: Distribution of the EDTA species, H_4Y , H_3Y^- , H_2Y^{2-} , HY^{3-} , and Y^{4-} , as a function of pH at 37 °C. In preparing this figure, the acid dissociation constants at 25 °C, from Table 3, have been extrapolated to 37 °C using Equation 19. Note that at the pH of the growth solution, the fraction of EDTA present as the fully deprotonated anion (Y^{4-}) is about 1×10^{-8} .

As indicated in Equation 29-31, in order to evaluate the competition between EDTA and the various phosphate ligands, for Al^{3+} cations, it is necessary to consider the equilibrium concentration of all species of EDTA (eg, the total or analytical concentration of unbound EDTA). Historical experience¹⁰ suggests that EDTA is present in “low impurity” KDP at levels that range between about 0.001 and about 0.03 mole% EDTA, relative to KDP.

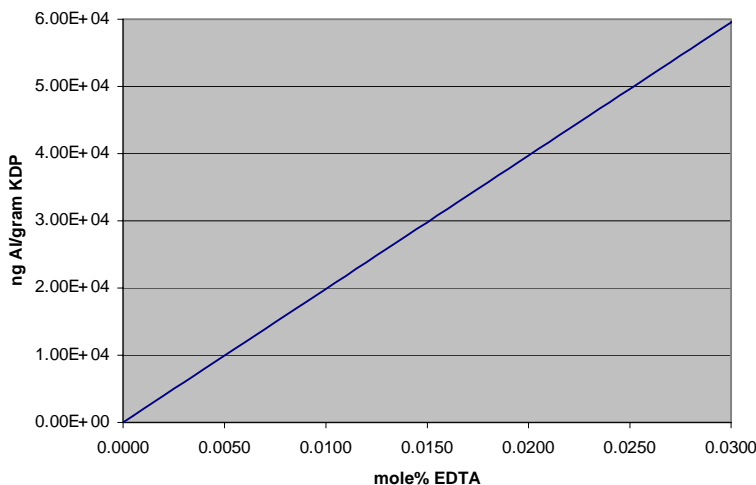


Figure 8: Stoichiometrically equivalent amounts of EDTA, given in mole% relative to KDP, and aluminum, expressed as ng Al/grams KDP. The levels of residual

¹⁰ David Wruck, and Richard Torres, LLNL, Personal Communication

EDTA in “low impurity” KDP have historically ranged between about 0.001 to 0.03 mole%.

As shown in Figure 8, the amount of aluminum that is stoichiometrically equivalent to these levels of EDTA ranges between 2000 ng Al/gram KDP and 60 μg Al/gram KDP. If we assume that all of the EDTA is available to bind with the Al^{11} , it appears that there has always been an excess of EDTA relative to Al.

If we assume a total concentration of Al of 1000 ng Al/g KDP then the minimum unbound EDTA would range between about 5×10^{-4} mole% and .03 mole%. Given a solubility of 2.1 moles KDP /liter at 37 °C, these values correspond to unbound (free) ligand concentrations of roughly 1×10^{-5} moles EDTA/l and 6×10^{-4} moles EDTA/l respectively. Because the EDTA is introduced as an impurity in the KDP feedstock, as additional KDP is dissolved the concentration of EDTA in solution also increases. For example at 70 °C the concentration of EDTA in solution may reach levels on the order of 1×10^{-3} moles EDTA/liter.

The competition between the EDTA and the phosphate anions for the Al^{3+} cations, at 37 °C is illustrated in Figure 9. For this example we have assumed a total free EDTA concentration of 2.2×10^{-4} moles EDTA/liter. This corresponds to an EDTA presence of 0.01 mole% in the KDP feedstock.

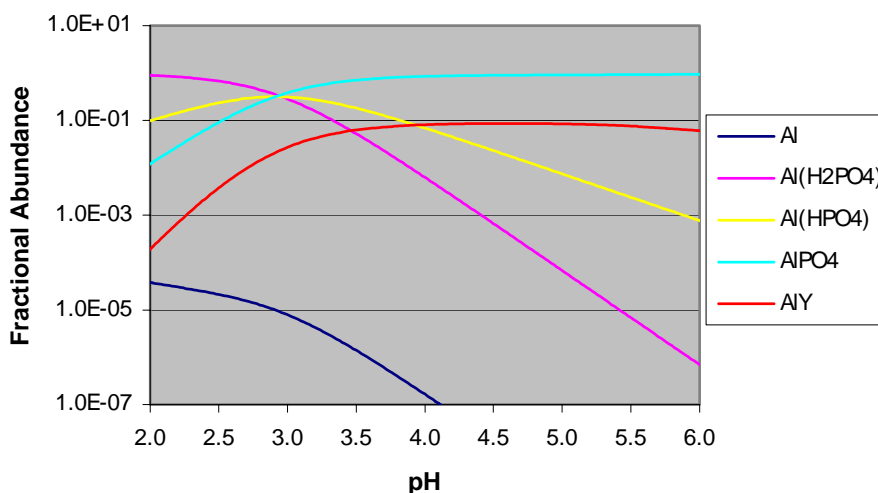


Figure 9: Distribution of aluminum species at 37 °C in the presence of a free EDTA concentration corresponding to 0.01 mole% EDTA relative to KDP. Under these conditions the relative abundance of each of the species is: AlPO_4 (85%), Al-EDTA^- (8 %), AlHPO_4^+ (5.2%) and $\text{AlH}_2\text{PO}_4^{2+}$ (0.4%).

¹¹ That is, we assume that there are no other cations present that form stronger complexes with EDTA than does Al. Such an approximation is most probably valid in the case of polymeric or polymer lined tanks. However, in glass tanks there may well be a sufficient quantity of cations having a higher formation constant leached from the tank to effectively sequester all of the EDTA present in solution.

As shown in Figure 9, at 37 °C, AlPO_4 remains the dominate species, accounting for about 85% of the total aluminum while the EDTA complex accounts for about 8% of the total aluminum. As shown in Table 3, the formation of the Al-EDTA complex is *endothermic*. This implies that the formation constant (K_f) of the Al-EDTA complex increases with increasing temperature. Unfortunately the heat of reaction (ΔH) for the formation of the aluminum phosphate complexes does not appear in the standard chemical thermodynamic compilations. Therefore, the temperature dependent nature of aluminum speciation cannot be considered in a straightforward manner.

One can, however, argue by analogy with other reactions that the formation of the dominant aluminum phosphates are most probably exothermic reactions. As such, the formation constants of these species would be expected to decrease with increasing temperature. Therefore as the temperature increased one would expect the Al-EDTA complex to become the dominant aluminum species. Consider for example the thermodynamics of Al-EDTA formation. Because the formation of the Al-EDTA complex is both endothermic and spontaneous one can immediately conclude that there must be an increase in entropy associated with this reaction. That is, ΔS must be positive. The magnitude of this increase in entropy can be calculated by combining the well-known relationship between ΔG and the equilibrium constant ($\Delta G = -RT\ln K$) with the definition of ΔG in terms of ΔH and ΔS . Using the values from Table 3 one finds that the formation of the Al-EDTA complex must entail an increase in entropy of 118 cal/mole-K.

Physically one can view this large entropy change as being the result of the increase in the number of independent particles created as a single (hexadentate) EDTA molecule binds to, and displaces the ordered solvent (water) sphere which surround each hydrated Al^{3+} cation¹². With a reaction involving a single dentate ligand such PO_4^{3-} (or HPO_4^{2-} or H_2PO_4^-) one would expect the entropy term (i.e. ΔS) to be much smaller than with a reaction involving a hexadentate ligand, such as EDTA. If, for a moment, one views the ΔS of 118 cal/mole-K associated with the formation the Al EDTA complex in terms of the number of water molecules displaced from the inner coordination sphere of the Al^{3+} cation one finds that there is a positive contribution to the ΔS term of approximately 20 cal/mole-K for each water that is displaced.

For comparison, the ΔS values for a variety of other aluminum complexation reactions are shown in Table 4. As shown in Table 4, one can postulate that the entropy of reaction is a simple function of the number of water molecules displaced from the coordination sphere. When this is done one finds that the entropy contribution appears to vary between about 15 and 30 cal/mole-K for each water molecule displaced. Using the formation constant for AlPO_4 at 37 °C (Table 2), and the rough correlation found in Table 4, implies that the ΔH for the formation of AlPO_4 would fall somewhere in the range between -17 and -13 kcal/mole. From Equation 19, the rate of change in the log of the formation constant ($\log(K_f)$) that would be implied by these enthalpies range between about 0.04/°C and -0.03/°C.

¹² F. Basolo and R.C. Johnson *Coordination Chemistry* W.A. Benjamin and Co. 1964 Pg. 129

Table 4: Entropy Terms Associated with the Formation of Various Aluminum Complexes⁶.

Reaction	S Cal/mole-K	S Cal/mole-K-water
$\text{Al}^{3+} + \text{F}^- = \text{AlF}^{2+}$	30	30
$\text{Al}^{3+} + 2\text{F}^- = \text{AlF}_2^+$	60	30
$\text{Al}^{3+} + 3\text{F}^- = \text{AlF}_3$	78	26
$\text{Al}^{3+} + 4\text{F}^- = \text{AlF}_4^-$	89	22
$\text{Al}(\text{OH})_2^+ + 2\text{OH}^- = \text{Al}(\text{OH})_4^-$	43	21
$\text{Al}^{3+} + 3\text{C}_2\text{O}_4^{2-} = \text{Al}(\text{C}_2\text{O}_4)_3^{3-}$	87	15

For convenience, let us assume an entropy of formation for each of the series of aluminum phosphate compounds that is near the upper end of the 15 to 30 cal/mole-K range that appears to be reasonable based on Table 4. For a value of 25 cal/mole-K for each reaction, the *postulated* heats of reaction and corresponding changes in log(K_f) are shown in Table 5.

Table 5: Postulated Heats of Reaction for the Formation of Al phosphate complexes

Reaction	Postulated ΔH kcal/mole	$\Delta \text{Log}(K_f)/^\circ\text{C}$
$\text{Al}^{3+} + \text{H}_2\text{PO}_4^- = \text{Al}(\text{H}_2\text{PO}_4)^{2+}$	1.7	0.004
$\text{Al}^{3+} + \text{HPO}_4^{2-} = \text{Al}(\text{HPO}_4)^+$	-3.2	-0.008
$\text{Al}^{3+} + \text{PO}_4^{3-} = \text{AlPO}_4$	-15	-0.036

Using these values, together with the experimentally determined heats of reaction shown in Tables 1 and 3, and the empirical expression for the solubility given in Equation 17 one can estimate the aluminum speciation at elevated temperatures in the presence of EDTA. The aluminum speciation at 65 °C in the presence of 0.01 mole% EDTA (relative to KDP) is shown in Figure 10. Because our knowledge of the temperature dependence of the aluminum phosphates is incomplete, the quantitative values shown in Figure 10 should be viewed with caution. None-the-less, comparison of Figures 9 and 10 illustrates the temperature-dependent disruption in aluminum speciation that one might reasonably expect to result from the introduction of modest quantities of residual EDTA.

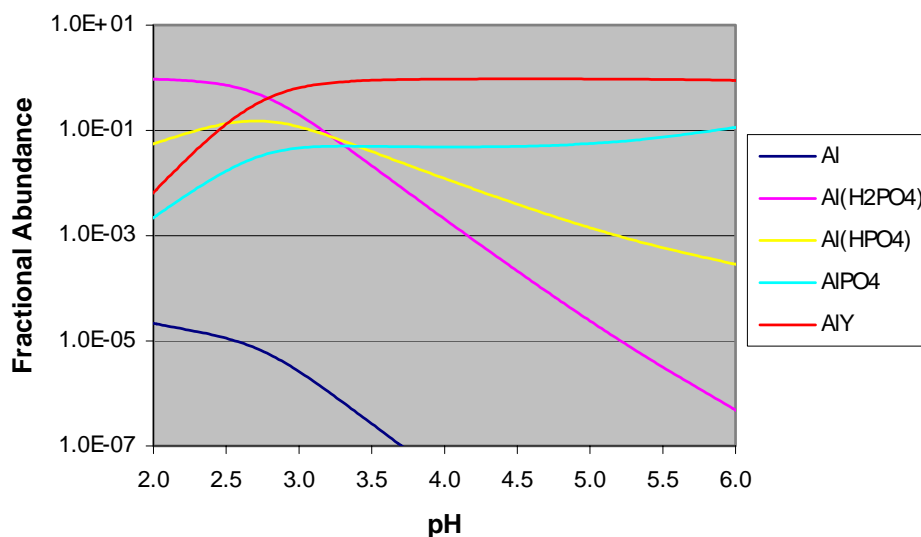


Figure 10: Distribution of aluminum species, at 65 °C in the presence of a free EDTA concentration corresponding to 0.01 mole% EDTA relative to KDP. The Al-EDTA species is denoted at AlY in the figure. In preparing this figure it has been assumed that the entropy of formation (ΔS) for each of the phosphate species is +25 cal/mole-K.

In addition to being a strong function of temperature, the competition of PO_4^{3-} and EDTA^{4-} anions for aluminum cations is also a function of the fraction of EDTA present in the KDP. In Figure 11 the fraction of AlPO_4 and Al-EDTA $^-$ (relative to total aluminum concentration) as functions of both temperature and EDTA concentration has been calculated. In preparing Figure 11 it has again been assumed that the enthalpy of formation for AlPO_4 is -15 kcal/mole. Additionally we have assumed that the EDTA is present in sufficient excess with respect to Al (and other impurities) such that the concentration of unbound EDTA is equal to the analytical concentration of EDTA.

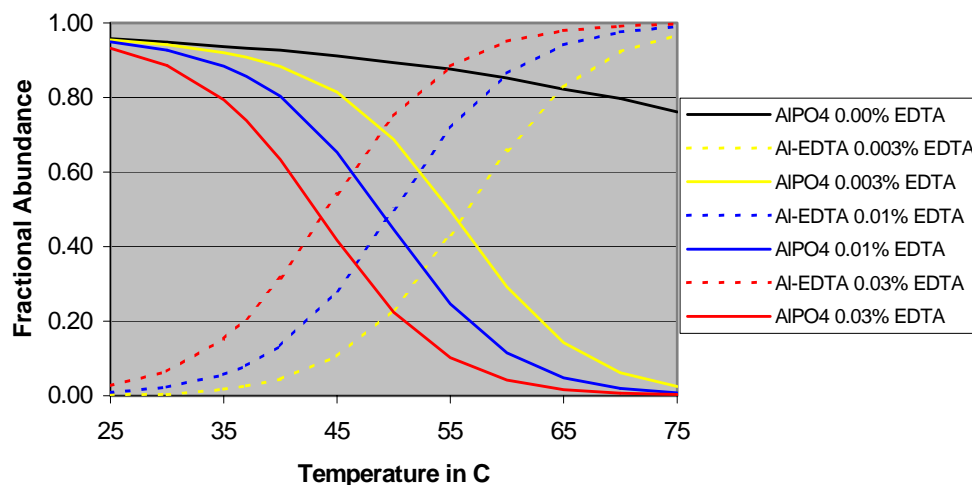
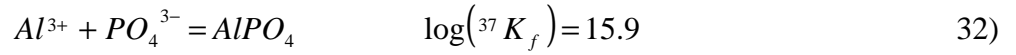


Figure 11: Fraction of Al-EDTA $^-$ (dotted lines) and AlPO_4 (solid lines) as a function of temperature and EDTA concentration. All EDTA concentrations are given in terms of mole% EDTA relative to KDP. Three EDTA concentrations are illustrated; 0.003% (yellow), 0.01%

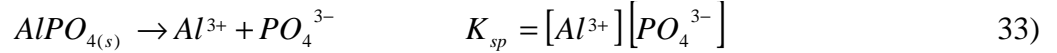
(blue) and 0.03% (red). Note that the fraction of $AlPO_4$ decreases with both increasing temperature and increasing EDTA concentration.

Solubility of Aluminum Complexes in Saturated KDP Solutions

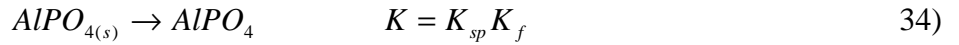
In the absence of EDTA one finds that the dominant solution phase aluminum species, at pHs typical of KDP growth, is $AlPO_4$. The formation of this species together with its formation constant (at 37 °C) can be represented by:



Because $AlPO_4$ is an uncharged complex one would expect that $AlPO_4$ would be only modestly soluble in aqueous solution. Customarily solubility equilibria are expressed in terms of a solubility product (K_{sp}):



At 37 °C, Smith and Martell⁶ give $\log(K_{sp})$ for $AlPO_4$ as -19.1 . By adding Equations 32 and 33 one can represent the equilibria that exists between the aqueous and solid phases of $AlPO_4$.



Thus at 37 °C, the logarithm (base 10) of the equilibrium constant describing the portioning of $AlPO_4$ between the soluble and insoluble phases (Equation 34) has a numerical value of -3.2 . That is, as one might expect, the formation of the solid phase is strongly favored.

Because trivalent cations, such as Al^{3+} , are sometimes added to KDP growth solutions as means of controlling the aspect ratio of KDP crystals it is of practical interest to estimate the solubility of aluminum salts in saturated solutions of KDP. That is, how much aluminum can be added before one risks the formation of a solid phase of $AlPO_4$? Let us define the solubility (in terms of moles per liter) of $AlPO_4$, as $^{AlPO_4}S$. By inspection of Equation 33, for each mole of $AlPO_4$ that dissolves, an equal number of moles of hydrated aluminum cations and phosphate ions will be formed. Once in solution both the hydrated aluminum cations and the phosphate anions will equilibrate such that for aluminum one can write:

$$^{AlPO_4}S = [Al^{3+}] + [AlH_2PO_4^{2+}] + [AlHPO_4^+] + [AlPO_4] + [Al-EDTA^-] + \dots \quad (35)$$

Similarly, in a saturated aqueous solution of KDP the phosphate species released by dissolution (or precipitation) of $AlPO_4$ will be insignificant in comparison to the phosphate species contributed by the dissolved KDP. Again multiple phosphate species can exist in solution, thus one can write:

$$^{KDP}S = [H_3PO_4] + [H_2PO_4^-] + [HPO_4^{2-}] + [PO_4^{3-}] \quad (36)$$

With respect to the thermodynamic force that drives Equation 33, only that fraction of aluminum that exists as Al^{3+} is of significance. Similarly, only that fraction of the total phosphate inventory that exists as the PO_4^{3-} ion is of significance. Further, by recognizing the effect that the pH of the solution has on the solubility of the KDP, one can express the solubility product (K_{sp}) from Equation 33 as:

$$K_{sp} = \frac{\alpha_3 \cdot A^{13+} \beta \cdot \text{AlPO}_4 S \cdot \text{KDP} S}{\sqrt{\alpha_1}} \quad (37)$$

Where:

α_1 is the fractional abundance of the H_2PO_4^- ion

α_3 is the fractional abundance of the PO_4^{3-} ion

β is the fractional abundance of the trivalent hydrated aluminum cation

Solving for the solubility of AlPO_4 one finds:

$$\text{AlPO}_4 S = \frac{K_{sp} \cdot \sqrt{\alpha_1}}{(\alpha_3 \cdot \text{KDP} S \cdot A^{13+} \beta)} \quad (38)$$

The solubility of AlPO_4 (Equation 38) at 37 °C has been evaluated for a saturated solution of KDP as a function of pH in Figure 12.

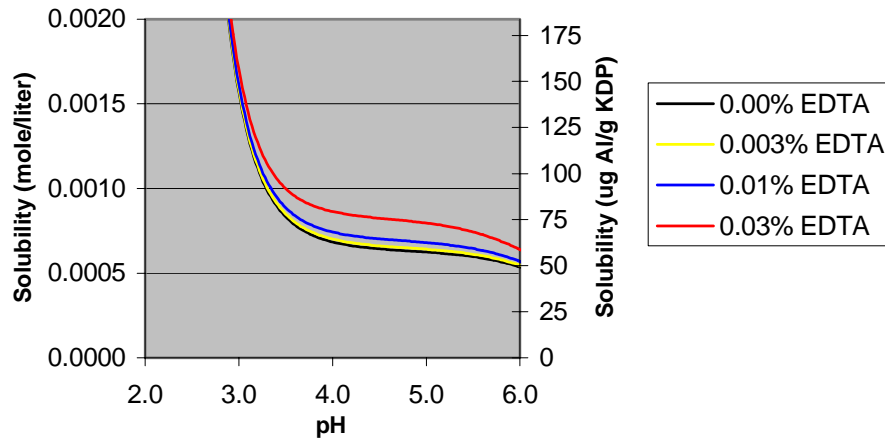


Figure 12: Solubility of AlPO_4 , at 37 °C as a function of pH and EDTA concentration in a saturated KDP solution. Note as the concentration of EDTA is increased the total solubility of Al increases, although not dramatically at this temperature.

As shown in Figure 12, at pHs of interest to KDP growth, Al is soluble to the extent of about 7×10^{-4} moles/liter. This corresponds to about 65 µg Al/gram of KDP at 37 °C. That is, at this temperature the equilibrium solubility limit for aluminum is considerably higher (by a factor of 30-

100) than the concentrations of Al that are typically present in growth solutions. Also notice that the presence of EDTA has only a modest effect on Al solubility at these temperatures. One would expect that the presence of EDTA would have a more pronounced effect on the solubility at elevated temperatures, where EDTA competes more effectively with phosphate for aluminum cations.

Summary and Conclusions Relevant to KDP Growth

Given the discussion above, the following points are of practical significance with respect to KDP crystallization:

The equilibrium pH of saturated aqueous KDP solutions lies in the range of 4.1 to 4.2. As the temperature of the solution is raised from 25 °C, the equilibrium pH becomes ever so slightly more basic. The pH of aqueous solutions of KDP is only modestly buffered by the presence of the conjugate acid (H_3PO_4) and conjugate base (HPO_4^{2-}) of the amphoteric dihydrogen phosphate (H_2PO_4^-). Comparatively modest deviations from the equilibrium pH would be expected to result in changes in the equilibrium solubility of KDP that are on the same order as the levels to which one typically tries to control super-saturation during the growth of single crystal KDP. For example, at 25 °C a deviation of 0.3 pH units will increase the equilibrium solubility of KDP by about 0.1%. Similarly, the equilibrium solubility of KDP will increase by about 0.5% in response to a deviation of 0.6 pH units from the equilibrium pH.

In the absence of EDTA, the dominant aluminum species in KDP growth solution would be expected to be AlPO_4 . Minor quantities of AlHPO_4^+ , and $\text{AlH}_2\text{PO}_4^{2+}$ would also be expected to be present. Introduction of small concentrations of EDTA (0.001-.03 mole% relative to KDP), at pHs of relevance to KDP growth, would be expected to result in a strong competition between the EDTA and the phosphate ion for the aluminum cations. Increasing the concentration of (unbound) EDTA would be expected to increase the fraction of the Al-EDTA complex, relative to the AlPO_4 complex.

Existing heats of reaction indicate that the formation of the Al-EDTA complex is strongly favored by increased temperatures. Although the temperature dependence of the reactions leading to the formation of the three aluminum phosphates are not known with certainty, there is good reason to suggest that the formation of AlPO_4 species is favored at lower temperatures (e.g. room temperature). If this is the case, reasonable arguments can be put forward to suggest that the speciation of aluminum might well be strongly disrupted, at elevated temperatures, by the presence of modest (0.001-0.03 mole%) concentrations of EDTA. Specifically, the presence of EDTA would be expected to have virtually no effect on growth solutions near room temperature, while at elevated temperatures a substantial fraction of the aluminum in solution would be expected to be present as the Al-EDTA, rather than as the AlPO_4 complex.

One would expect that the speciation of a given metallic ion or complex in solution would profoundly effect the ability of such a species to interact with a crystal, and thus influence its growth rate. Thus the competition between the phosphate and the EDTA, for aluminum

cations, has a number of practical implications with respect to KDP growth. First, phenomenological parameters, such as the segregation coefficient (i.e. the concentration of Al in the crystal relative to the concentration of Al in solution) would be expected to show temperature dependence. If, for example, AlPO_4 were the species which most strongly interacts with the crystal lattice one would expect the segregation coefficient to decrease in proportion to the fraction of AlPO_4 in solution for a given total aluminum concentration. In the absence of EDTA, such a reduction would be expected to be relatively modest (see Figure 11). Using the temperature dependence described above, one finds that the fraction of AlPO_4 in solution drops from about .96 at 25 °C to about .82 at 65 °C (see Figure 11). In the presence of residual EDTA, however, a much more substantial temperature dependence might be expected. For example, with a salt containing 0.01mole% EDTA the fraction of aluminum present as AlPO_4 is about 95% at 25 °C, it is only about 5% abundant at 65 °C. Thus, other things being equal, the total concentration of Al that would be required to affect a specific crystal aspect ratio for a crystal grown at 25 °C would be quite different than the total concentration needed to achieve the same degree of prismatic pinning, and thus aspect ratio at 75 °C.

The fate of Al in KDP growth runs, containing EDTA, that are conducted in glass tanks is quite complicated. For example, since glass tanks typically leach a variety of cations, the concentration of unbound EDTA ligand may be strongly reduced by the presence of cations having larger formation constants than Al. Such ions would be expected to sequester the EDTA present, preventing it from forming complexes with Al^{3+} . Examples of such cations would include most of the tri and tetravalent cations, including, Bi^{3+} , Fe^{3+} , Ga^{3+} , In^{3+} , Th^{4+} , Zn^{3+} , as well as many divalent metals¹³, including Cu^{2+} , Pb^{2+} , Ni^{2+} , Zn^{2+} . Potentially such a technique could be used to advantage to sequester the residual EDTA commonly found in "high purity" KDP feedstock. Complexing the residual EDTA with an excess of a metal known not to incorporate into either the prismatic or pyramidal face of the KDP might provide a means of preventing the residual EDTA from perturbing the equilibria involved with common trivalent ions (such as Al^{3+}) that are intentionally added to influence crystal aspect ratio. Alternately the level of residual EDTA might be strongly reduced by re-crystallization of the feedstock prior to use in single crystal growth runs.

Finally, the present work suggests that at the low pHs typically used for growth of KDP that the solubility of aluminum is limited by the equilibria between the aqueous phase AlPO_4 and solid phase AlPO_4 . At 37 °C the equilibrium solubility of AlPO_4 is about 7×10^{-4} moles AlPO_4 /liter of saturated KDP. This is equivalent to about 65 µg Al/gram of KDP at saturation.

Acknowledgement

The author extends his appreciation and thanks to a number of colleagues, particularly Bill Bourcier, Alan Burnham, Rich Torres, Ruth Hawley-Fedder and Bill Mclean, for their close reading and useful comments on early drafts of this memorandum.

¹³ Louis Meites, *Handbook of Analytical Chemistry First Edition*, McGraw Hill Book Company 1963 page 3-89

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